

NONAQUEOUS-PHASE LIQUID CHARACTERIZATION AND POST-REMEDiation VERIFICATION SAMPLING

Charles Tabor (Charles.tabor@gjo.doe.gov), Randall Juhlin, and Paul Darr (S.M. Stoller Corporation, Grand Junction, Colorado USA)
Julian Caballero and Joseph Daniel (S.M. Stoller Corporation, Largo, Florida USA)
David Ingle (U.S. Department of Energy, Largo, Florida USA)

ABSTRACT: Light and dense nonaqueous-phase liquids (NAPLs) were identified in the surficial aquifer at the Northeast Site of the Young-Rainey Science, Technology, and Research Center located in Largo, Florida. The composition and the horizontal and vertical extent of NAPLs were determined using historical site information, analysis of ground water and soil boring data, and analysis of free product recovered from wells. Trichloroethene, dichloroethene, methylene chloride, toluene, and oils were identified as NAPLs. Calculations were conducted to determine NAPL remediation goals for both soil and ground water. Following completion of in situ thermal remediation activities at a 9,900-cubic-meter NAPL contamination area, a sampling program was implemented to verify the success of the remediation. The program consisted of using hot media sampling techniques to collect soil and ground water samples at randomly chosen locations in three sampling events during a 6-month period. Verification data indicate that the remediation was successful.

INTRODUCTION

The Young-Rainey Science, Technology, and Research (STAR) Center, located in Largo, Florida, is the location of a former U.S. Department of Energy (DOE) facility (the Pinellas Plant) that produced components for nuclear weapons from the mid-1950s until 1995. The site was sold in 1995, but DOE remains responsible for environmental restoration activities resulting from historical DOE production operations. The Northeast Site at the STAR Center contains an area that was used for waste solvent staging and storage prior to 1968. Debris excavation in 1995 resulted in the removal of 241 drums or drum pieces from a maximum depth of 1.8 meters (m) below land surface. The drums contained solvent, liquid and solidified resin, soil, scrap components and parts, and unidentified viscous liquids. Debris such as concrete and lumber was also removed during the excavation.

Ground water at the Northeast Site occurs in a shallow surficial aquifer consisting of approximately 9 m of fine silty sand with varying amounts of clay and some shelly layers. Underlying the surficial deposits is a 21-m-thick clay layer that acts as an aquitard. The ground surface is essentially flat, and the depth to ground water ranges from 0.3 to 1.8 m below land surface, varying with rainfall volumes. Horizontal hydraulic conductivity ranges from approximately 3.5×10^{-4} to 2.5×10^{-3} centimeter per second, and vertical hydraulic conductivity ranges from 1.1×10^{-6} to 1.1×10^{-4} centimeter per second. The hydraulic gradient is low, resulting in pore water velocity estimates that range from 3 to 6 m per year.

NAPL CHARACTERIZATION

Very high contaminant concentrations indicative of NAPL were observed in ground water samples collected from some monitor and ground water recovery wells that were installed following the debris removal. An effort was made to confirm NAPL presence by using a peristaltic pump to collect liquid samples from the water table surface and from the bottom of these wells. One well produced approximately 23 liters of NAPL, and other wells produced lesser volumes of NAPL. NAPL was observed to occur in both light (LNAPL) and dense (DNAPL) forms (Figure 1). In some samples, multiple LNAPL or DNAPL layers were observed. Samples were submitted to an analytical laboratory where the liquid layers were separated and analyzed. The analytical methods applied included U.S. Environmental Protection Agency (EPA) SW-846 8260 (volatiles) plus tentatively identified compounds, 8270 (semivolatiles) plus tentatively identified compounds, and 8100 Modified (hydrocarbon fractions). American Society for Testing and Materials methods for petroleum distillation (D86) and liquid density were also employed. The D86 method was applied in anticipation of using a thermal technology to remove the NAPLs from the subsurface.

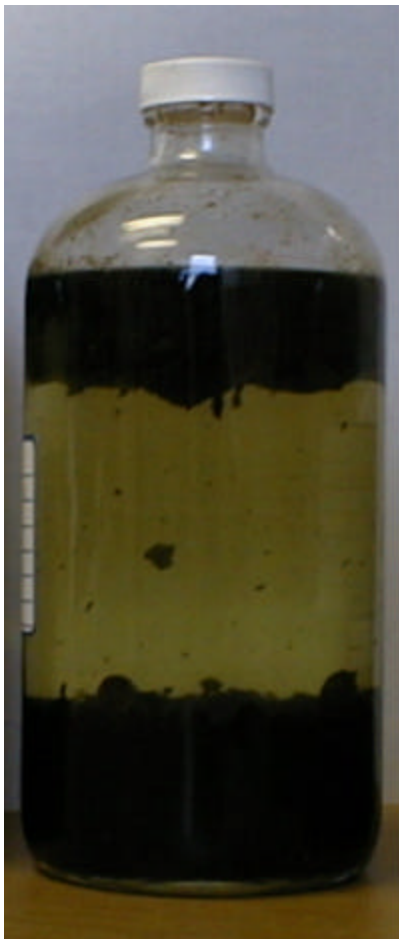


FIGURE 1. Site sample showing LNAPL (top), water (middle), and DNAPL (bottom) layers.

Analytical results indicated a complex mixture of chlorinated and aromatic solvents and oils, with the NAPL composition varying widely from location to location. Trichloroethene (TCE), *cis*-1,2-dichloroethene (DCE), methylene chloride, and toluene were present in the NAPL in fractions ranging from 3% to 55%. Significant fractions (40% to 55%) of hydrocarbons as heavy oils were also present in some NAPL samples. Although *cis*-1,2-DCE usually is considered a transformation product of tetrachloroethene or TCE degradation, it appears likely that this contaminant entered the subsurface directly as a NAPL at the Northeast Site. Evidence for this includes the listing of DCE as a solvent used historically at the site, the presence of DCE in the recovered NAPL, the presence of DCE in ground water at concentrations up to 30% of its aqueous solubility, and the presence of high DCE concentrations in soil and ground water at locations where tetrachloroethene or TCE has never been detected.

DNAPL layers contained dense solvents like TCE and methylene chloride but also contained significant fractions (up to 40%) of light solvents like toluene. Some LNAPL layers also contained TCE. The LNAPL and DNAPL compounds either were mixed together in the drums or became naturally mixed after migrating into aquifer sediments. Results of liquid density tests showed that the density of the LNAPL layers ranged from 0.902 to 0.969 gram per milliliter, and the density of oily

DNAPL layers ranged from 1.01 to 1.03 gram per milliliter. The density of non-oily DNAPL samples (containing mostly solvents) was not measured, but these DNAPLs likely had a higher density than the oily DNAPLs.

Given the presence of NAPLs in the surficial aquifer, a program was undertaken to characterize the horizontal and vertical extent of the NAPLs. Historical information about solvents and other materials used at the site were reviewed. Although information concerning historical drummed waste disposal during plant operations was limited, data collected during debris removal provided a starting point for the investigation. In addition, historical data from monitor and ground water recovery wells were used to evaluate the potential presence of NAPLs. If the concentration of a particular contaminant in ground water exceeded 1% of the contaminant's aqueous solubility, it was assumed that the contaminant could be present as a NAPL.

In addition to the historical data, various other characterization methods were considered for assessing NAPL distribution. At the time (1998–1999), this evaluation indicated that the collection and analysis of soil cores would be most beneficial for identifying NAPL extent, particularly when applied in combination with the review of ground water data and historical site information. Collection of soil cores was conducted in two phases: the first in December 1999 and January 2000 and the second in June 2000.

Direct-push, hollow-stem auger, and sonic drilling techniques were used to collect soil cores from selected areas. Depending on the drilling method, continuous cores were collected in 0.6-, 1.2-, or 1.5-m intervals, with the shallowest collected 1.5 m below land surface. Core collection generally extended a few meters into the clay layer underlying the surficial aquifer. Care was taken to ensure effective isolation of the surficial sediments from the underlying clay to prevent potential downward NAPL migration. Sonic drilling provided (1) fast and efficient penetration into the clay layer, (2) cost-effective surface casing isolation, and (3) nearly complete core retention of hard materials. Initial plans were to collect samples from a maximum depth of 1.5 m into the clay layer, but sample collection was expanded to 3 to 4.5 m into this layer because results of the initial phase of the investigation indicated that contamination existed in the clay.

Soil cores were screened with a photoionization detector to identify the section of the core with the highest organic vapor concentration. This information, along with visual observations of the core, was used to select a sample location within each core interval. At a minimum, samples were collected approximately every 0.5 to 0.9 m in the surficial sediments and every 0.6 to 1.8 m in the clay layer. Lithologic logs produced for each boring location assisted in data interpretation.

Analysis of data from the first phase of soil core collection made it possible to focus on key areas during the subsequent second phase. Initially, an on-site mobile laboratory was used to analyze core samples in hopes of getting near-real-time data, but sample analysis could not keep pace with sample collection, and this approach was not used in the second phase of the investigation.

DEVELOPMENT OF NAPL REMEDIATION GOALS

The determination to use a thermal technology was made following an assessment of all commercially available NAPL remediation technologies. Proposals from thermal technology vendors were evaluated, and the combination of steam injection and electrical heating was selected as the best option for this site.

Various approaches were considered for evaluating the performance of the thermal NAPL remedial action at the Northeast Site. An approach commonly used in the past has been to estimate total NAPL mass in the subsurface prior to remediation, and then compare the mass of NAPL recovered with this estimate. A review of the literature and discussions with practitioners involved in NAPL remediation indicated that this approach has a significant shortcoming: the uncertainty of the initial NAPL mass estimate. If the estimate is larger than the actual mass, the mass removal goal cannot be met.

Ultimately, the decision was made to use media-specific and contaminant-specific remediation goals to evaluate the performance of the NAPL remediation. Contaminant concentrations measured in soil and ground water samples collected after the action would be required to meet these specified concentrations for the remedial action to be considered successful.

The calculations used to develop the remediation goals for specific NAPL compounds were in large part based on methods that have historically been used to assess the potential presence of residual NAPL (Feenstra et al. 1991; EPA 1991; Cohen and Mercer 1993; Pankow and Cherry 1996). These methods apply the principle of equilibrium partitioning between phases to calculate a theoretical pore water concentration that is then compared to the effective solubility of the contaminant. The steps involved in this process require an analysis or estimate of the composition of the NAPL, which in turn is used to calculate the mole fraction and the effective solubility of each NAPL component.

Initial calculations to determine the effective solubility of individual contaminants were problematic because of significant spatial variations in NAPL composition. These variations produced a wide range of calculated mole fractions and effective solubility for each contaminant. For example, the effective solubility of TCE varied from approximately 20 to 500 milligrams per liter. Given that the ranges of calculated effective solubility for other contaminants were similarly large, it was difficult to choose a single value of effective solubility for each contaminant against which site-wide aqueous-phase concentrations could be compared to assess the presence of NAPL.

Analysis of the NAPL calculations showed that the effective solubility of each of several contaminants that constituted the smallest mole fractions of NAPL tended to equate to a few percent of the contaminant's full aqueous solubility. Because these contaminants were assumed to be present as NAPL, the decision was made to use 1% of each contaminant's full solubility as the threshold for assessing NAPL presence (i.e., NAPL was assumed to be present wherever aqueous-phase concentrations were above this value, but absent where aqueous-phase concentrations fell below this value). Accordingly, the aqueous-phase remediation goal for each contaminant was set equal to 1% of its full solubility (Table 1).

TABLE 1. Ground water and soil remediation goals.

NAPL Component	Ground Water Remediation Goals (micrograms per liter)	Soil Remediation Goals (micrograms per kilogram)
TCE	11,000	20,400
<i>cis</i> -1,2-DCE	50,000	71,000
Methylene Chloride	20,000	227,000
Toluene	5,500	15,000
Total Petroleum Hydrocarbons ^a	50,000	2,500,000

^a Remediation goals not determined using solubility and equilibrium calculations.

To determine the soil remediation goals, the principle of equilibrium partitioning between phases (e.g., Cohen and Mercer 1993) was used to calculate soil concentrations that were equivalent to the aqueous-phase goals (Table 1). The final soil remediation goals were calculated using a soil organic carbon content value that was an average of the data from a subset of the soil cores collected during NAPL delineation.

The remediation goals for the oil NAPLs were not determined in the same manner as the goals for the specific compounds. The total petroleum hydrocarbons parameter was chosen to represent the oils during analysis. The values chosen for remediation goals were determined by reviewing literature and discussing the issue with colleagues.

The remediation goals presented in Table 1 for the individual compounds might initially be perceived as being conservatively low. However, it was determined that they were reasonable given that the effective solubility of an individual NAPL component can be substantially smaller than its full solubility. Regardless of the relative conservatism built into the computed goals, they were believed to be appropriate for the Northeast Site.

VERIFICATION SAMPLING

Characterization activities identified two distinct areas containing NAPLs, Area A and Area B. Active heating of Area A began in October 2002 and ended in January 2003. Following completion of active heating, a sampling program was implemented to verify that remediation goals had been met. This program consisted of three sampling events, one each at 6, 12, and 24 weeks after the end of active heating. Temperature monitoring was conducted after the end of active heating to ensure that subsurface temperatures were below 100°C prior to the first sampling event.

Locations for verification sampling were selected using a grid approach (EPA 1989). It was estimated that 16 soil and 16 ground water sampling locations would be sufficient to characterize the 930-square-meter remediation area; consequently, a grid consisting of 16 cells that each measured 7.6 by 7.6 m was overlain on a map of the site. Random number generation was used to select the x and y coordinates for the location of a temporary ground water monitor well and a soil boring within one of the cells. This same configuration was applied to the other 15 cells (Figure 2). Because the piping and wiring infrastructure was still in place at the time of the first sampling event, several of the designated locations were moved to accommodate access by a direct-push drilling rig.

The temporary monitor wells had 1.5-m screened intervals at randomly selected depths. The first soil sample depth at each soil sampling location was also selected randomly. This depth fell within the range of 0.3 to 2.4 m below land surface, and additional samples were collected at 2.4-m intervals below that depth. Ground water samples were collected from the 16 monitor wells during all sampling events. Soil samples were collected from the surficial aquifer sediments during the first event and from the clay layer during the second event.

Sampling was also conducted at locations just outside the perimeter of the remediation area to monitor for potential contaminant mobilization during the remediation activities. Four well pairs (deep and shallow) were sampled before, during, and after the remedial action, and four soil boring locations were sampled subsequent to the remedial action (Figure 2).

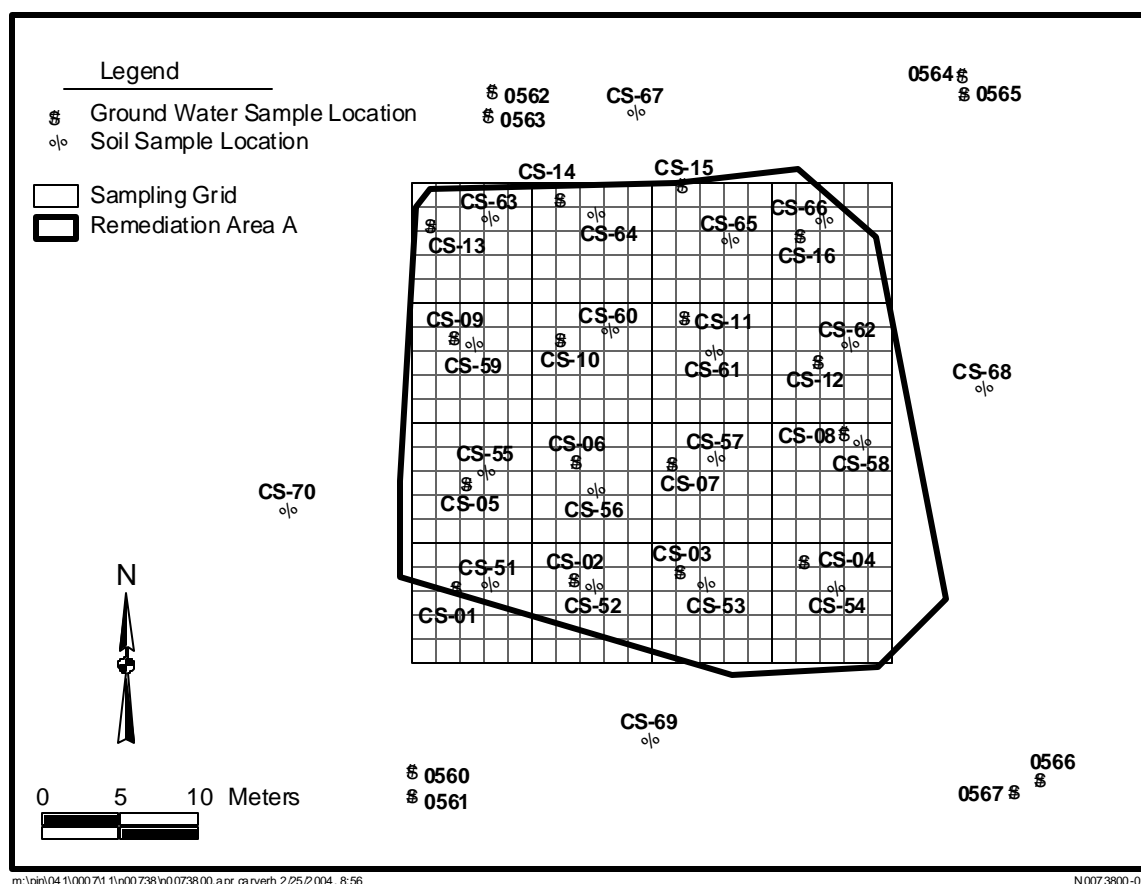


FIGURE 2. Verification sample locations.

Hot sampling techniques were used to collect samples. Hot ground water samples were collected by placing Teflon[®] tubing down the well to the middle of the screened interval and purging at the surface with a peristaltic pump. The Teflon[®] tubing ran first to a stainless steel coil submerged in an ice chest, then connected to the silicone pump tubing, and then to a flow cell containing instrumentation used to measure ground water parameters to determine when stability was reached during purging. Ground water samples were then collected using the pipette method.

A Geoprobe was used to collect hot soil cores from the surficial sediments into stainless steel core tubes. Cores were capped immediately and cooled by placing them on ice. After cooling, the core tubes were opened, and a sample was collected using a syringe-type sampler. Soil and ground water samples were submitted to an analytical laboratory for analysis of volatile organic compounds and total petroleum hydrocarbons.

A statistical approach was used to evaluate the contaminant concentration data from soil and ground water samples in terms of meeting the remediation goals (EPA 1989). Remediation success was interpreted to mean that 90% of the site met the remediation goals with a 90% certainty. No soil sample could have a contaminant concentration that exceeded a remediation goal by more than 100%, and no ground water sample could have a contaminant concentration that exceeded a remediation goal by more than 50%. For soil samples collected in the clay layer, no more than 50% of the samples could

exceed a remediation goal. This approach allowed a few samples to exceed the remediation goals by a small amount while ensuring that the bulk of the area met the goals.

Results of the three verification events demonstrated that remediation goals were achieved at all sampling locations. Contaminant concentrations in ground water samples were very low (near drinking water maximum contaminant levels) and soil results were also very low. Juhlin et al. present a summary of the entire NAPL remediation project in these conference proceedings.

ACKNOWLEDGMENTS

This work was performed under DOE contract number DE-AC01-02GJ79491 by the S.M. Stoller Corporation for the U.S. Department of Energy, Office of Legacy Management, Grand Junction, Colorado.

REFERENCES

- Cohen, R.M., and J.W. Mercer. 1993. *DNAPL Site Evaluation*. C.K. Smoley and CRC Press, Boca Raton, Florida.
- Feenstra, S., D.M. Mackay, and J.A. Cherry. 1991. "A Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples." *Groundwater Monitoring Review*, Volume 11, Number 2.
- Pankow, J.F., and J.A. Cherry. 1996. *Dense Chlorinated Solvents and Other DNAPLs in Groundwater: History, Behavior, and Remediation*. Waterloo Press, Portland, Oregon.
- U.S. Environmental Protection Agency. 1989. *Methods for Evaluating the Attainment of Cleanup Standards, Volume 1: Soil and Solid Media*. EPA 230/02-89-042.
- U.S. Environmental Protection Agency. 1991. *Estimating Potential for Occurrence of DNAPL at Superfund Sites*. EPA 9355.4-07FS.